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AUTHORITY

AFRPL ltr dtd 7 May 1973 AFRPL ltr dtd 7 May 1973

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BY

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(TITLE UNCLASSIFIED) EVALUATION OF HIGH-ENERGY BINDER

P. L. Allen
E. K. Ives
R. M. Kumagai
L. K. Asaoka
United Technology Center

TECHNICAL REPORT AFRPL-TR-66-255 September 1966

Group 4

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FOREWORD

- (U) This report is the second of three quarterly reports on Contract No. AF 04(611)-11404 under which United Technology Center (UTC) is conducting a program to evaluate the high-energy NF₂ binder, PBEP, in prototype propellant formulations. This report covers the experimental work conducted at UTC's Sunnyvale, California, research laboratories during the period 1 June 1966 through 31 August 1966. The work performed under this project is in response to requirements of AFFTC Project 3148, Program Element No. 62405184, BPSN 623148. Approving authority is Mr. Robert C. Corley, RPCS, AFFTC, Edwards Air Force Base, California.
- (U) Publication of this report does not constitute Air Force approval of the findings or conclusions presented herein. It is published only for the exchange and stimulation of ideas.

Approving authority is Mr. Corley

CONFIDENTIAL ABSTRACT

Thermal stability of PBEP and PBEP propellant and the effect of various additives on stability were studied. Excesses of the curative, TDI, or crosslinker, 1,2,6-hexanetriol, and most AP burning rate catalysts increased the weight loss of PBEP and PBEP propellants. Tricresyl phosphate, resorcinol, and sulfur all improved the thermal stability of the propellant with tricresyl phosphate giving the greatest improvement. The use of aluminum hydride (AlH3) continues to look promising in PBEP propellant. Good cures were obtained in a HAP/AlH3/PBEP/TVOPA system. The impact and friction sensitivities of the AlH3 propellants remain undesirably low. rates of 2.6 in./sec at 1,000 psi were obtained by conventional techniques. The obtaining of a low burning rate PBEP propellant will probably depend upon methods of reducing the decomposition rate of the binder during combustion. Cure problems were encountered in scaling up PBEP propellant to a two-quart mixer. Work is continuing to achieve a satisfactory cure.

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ABBREVIATIONS AND SYMBOLS

1,2,6-HT 1,2,6-hexanetriol

AlH₃ aluminum hydride (C)

AP ammonium perchlorate

Bu₂SnAc₂ dibutyl tin diacetate

DTA differential thermal analysis

FeAA ferric acetylacetonate

Fe₂O₃ ferric oxide

HAP hydroxylamine perchlorate

Lif lithium fluoride

MgO magnesium oxide

N₂F₄ tetrafluorohydrazine

NF₂ nitrogen difluoride

PBEP poly 1, 2-bis(difluoramino)2, 3-epoxy propane (C)

QMB-3 tetramethyl ammonium hydrotriborate, a product

of Callery Chemical Company

TDI tolylene diisocyanate

TVOPA 1, 2, 3-tris [1, 2-bis (difluoramino) vinoxy] propane (C)

XL crosslinked

SECTION I

INTRODUCTION

1. PROGRAM SCOPE

- (C) Under Contract No. AF 04(611)-11404, UTC is conducting a research program to evaluate a high-energy NF₂ binder in both metallized and non-metallized propellints oxidized by conventional and high-energy oxidizers. The purpose of the program is the extension of the utility of the PBEP binder with state-of-the-art fuels and advanced fuels to yield advanced propellants of high performance, high densite and high-performance efficiency. In addition to these objectives, e program also is designed to develop a high burning rate NF2 propellant and to provide test data on the stability of NF₂ propellants. Work under this contract began on 1 March 1966.
- (C) The program is divided into three phases. Phase I is concerned with the development of propellants with aluminum and boron as fuels. Phase II is devoted to the exploitation of the PBEP binder as a high-energy replacement for existing high-performance systems. Aluminum hydride, beryllium, and beryllium hydride fuels are to be formulated with a variety of oxidizers and plasticizers. Phase III is devoted to the development of techniques for measuring the stability of NF₂ propellants and for the characterization of these propellants using manometric and physical deterioration measurements.
- (C) The primary goals of this work are:
 - A. Development of a boron and aluminum propellant with a theoretical impulse of 300 sec
 - B. Development of a propellant with an impulse greater than current state of the art (265 sec) and a density greater than 0.065 lb/in.³
 - C. Development of a propellant with a burning rate range of from 1.0 to 10.0 in./sec at 1,000 psi

D. Obtain data on the long-term aging stability of Domino propellants based on the PBEP binder.

2. REPORT STATUS

(U) The present report covers the experimental work performed during the second quarter, 1 June 1966 to 31 August 1966. The reporting status for the program is presented graphically in figure 1.

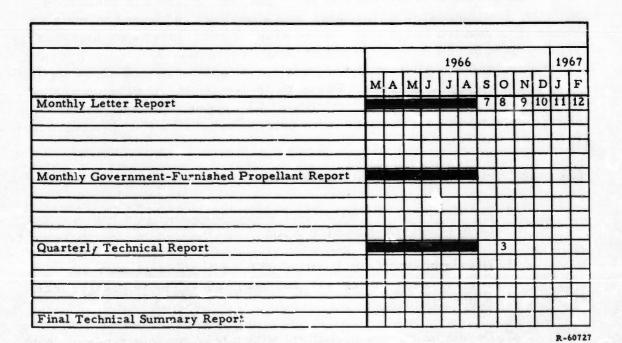


Figure 1. (U) Program Report Status

SECTION II

TECHNICAL DISCUSSION

- (C) PBEP is prepared by Shell Chemical Co. by the direct addition of N_2F_4 to the unsaturated carbon-to-carbon double bonds in dehydrochlorinated polyepichlorohydrin which has been glycerol initiated. PBEP is a tancolored, highly viscous polymer with a typical molecular weight for the current material of 3,300 to 3,800.
- (C) Formulation of PBEP propellants is accomplished by addition of a plasticizer to lower the viscosity of the prepolymer. The polymer is hydroxy-terminated and is cured with an isocyanate such as TDI used in conjunction with a crosslinker such as 1, 2, 6-hexanetriol.

1. PBEP STABILITY STUDIES

- (C) Difluoramino compounds have a history of marginal thermal stability. This is one of the areas of critical importance in the development of a PBEP propellant. To evaluate fully the stability of PBEP propellants, thermal stability studies of the next PBEP as well as of PBEP propellant are underway. In addition to this basic evaluation of stability, the effects of additives such as curatives, burning rate modifiers, and stabilizers are being studied.
- a. PBEP Decomposition Study by Mass Spectrograph
- (C) An attempt was made to identify the gaseous decomposition products of FBEP by mass spectrographic analysis of gaseous products from the decomposition of PBEP at 70° to 85° C. The initial study was conducted throughout this temperature range to obtain the maximum information from one analysis within a reasonable period of time.
- (U) To obtain the sample, a 15-cc stainless-steel cylinder was connected to a stainless-steel collection trap with appropriate valves, pressure-vacuum gauge, and lines. The system was pacified by an HF flush and then checked for leaks under vacuum over a 48-hr period. A 2-g PBEP sample in a small polyethylene vial was placed in the sample cylinder and the

system thoroughly purged with argon. The system was conditioned in a constant temperature bath at 29.5-in. Hg vacuum. After each exposure of 70°, 75°, 80°, and 85° C the gaseous decomposition products were collected in a liquid nitrogen trap. The connecting lines were flushed by argon-vacuum cycles before each collection.

- (U) The changes in pressure at these temperatures correlated with decomposition observed previously in TGA analysis. The heated PBEP sample had darkened with an increase in volume caused, perhaps, by trapped gases.
- (C) The mass spectrum of the gas sample was obtained with a CEC Model 21-103C mass spectrometer by Stanford Research Institute. The results are listed below. Quasi-quantitative values are given only to indicate relative orders of abundance.

Component	mol-%	Component	mol-%
H ₂	48	co ₂	4
H ₂ O	14	Air	7
N_2 , C_2H_4 , CO	15	C ₆ H ₁₄ (branched)	3
CH ₂ Cl ₂	8	HF	0.1
Unidentified	1		

- (U) Also, the gas was sampled after evacuation at liquid nitrogen temperature, but the spectrum showed no difference except in the loss of hydrogen and air.
- (C) The lack of HF and high percentage of H₂ is probably caused by the interaction of HF with the steel walls of the container. The presence of the branched hydrocarbon as well as CO₂, and possibly C₂H₁ and CO, indicates some degradation of the polymer backbone.
- b. Effect of PBEP Curing Additives
- (C) Differential thermal analysis (DTA) results indicate that a large percentage of the cure additives FeAA, TDI, and 1, 2, 6-hexanetriol decrease the stability of PBEP. PBEP Lot 9165-107 samples with these additives were conditioned at 45° C and the weight losses measured.

There has been some evidence also that the polyurethane linkage in the PBEP/TVOPA binder causes instability. Therefore, the unethanes of methyl alcohol and TDI and DDI were added to PBEP to determine the effect of the unethane linkages on stability. As shown in table I, there is definite evidence that the unethane linkage causes some instability. The large weight loss with TDI possibly is caused by volitization of the excess TDI. The instability induced by the unethanes is, however, significantly less than that induced by excess FeAA or 1, 2, 6-HT.

c. Stabilizing PBEP by Additives

- (C) Aerojet-General has screened a large number of ingredients as additives to improve thermal stability of their TVOPA/polyurethane propellan.. At 0.5 wt-%, K₃PO₄, Na₂SeO₃, and Na₃PO₄ were found to be the best stabilizing additives. United Technology Center has conducted DTA tests to screen possible candidate stabilizers. Table II lists the results of tests conducted for 72 days at 45° C. Tricresyl-phosphate was found to be the best stabilizer with resorcinol and Ca₃PO₄ running second.
- (C) Sulfur is known to be a polyurethane s'abilizer. A sample of UTX 8407 with 2% sulfur was conditioned at 60° C for 111 days. The results in table III show that there is some improvement. Urea and Lif, which are candidate burning rate modifiers and/or stabilizers also were tested and found to be ineffective as stabilizers.

d. Effect of Burning Rate Catalysts

(C) Weight loss measurements made of samples of UTX 8407 with 1% of each of four burning rate catalysts are shown in table IV. All of these accelerated the decomposition loss rate. Cured PBEP/TVOPA binder and cured PBEP samples also were tested for comparison purposes.

e. PBEP Propellant Diffusion Tube Specimens

(C) Stability samples employed at UTC initially were 3 cm in diameter and approximately 2 g in weight, or about 2 to 3 mm in depth. Because formulations with relatively high vapor pressures are affected by the propellant path or web that the decomposition gases or volatiles must pass through, surveillance studies were initiated with samples 1 cm² in cross section and 5 cm in length. UTX 8407, the standard Al/AP/PBEP/TVOPA, has a weight loss of 0.16% at ambient after 200 days and 0.67% at 45° C after 200 days, as listed in table V. Some swelling of the samples was observed at 45° C after approximately 100 days. UTP 8298, a 50% TMETN-plasticizer polyether binder, lost 0.044% at ambient and 2.25% at 45° C for the same period. The effect of plasticizer volatility was

TABLE I

(U) EFFECT OF CURE ADDITIVES ON PBEP STABILITY

68 Days at 45° C

	Wt-% Loss
PBEP (lot 107) neat	(1) 2.34 (2) 2.37
PBEP (lot 107) + 10% 1, 2, 6-HT	8.01
PBEF (lot 107) + 10% FeAA	8.82
PBEP (lot 107) + 10% TDI	14. 39
PBEP (lot 107) + 10% MeOH/DDI urethane	3. 62
PBEP (lot 107) + 10% MeOH/TDI urethane	4. 75

TABLE II

(U) EFFECT OF SELECTED STABILIZERS ON PERCENT WEIGHT LOSS

Exposure Time = 72 Days at 45° C

Order of Effectiveness	0.5% Additive to Basic UTX 8407 Formulation	Wt-% Loss
i	Tricresylphosphate	0.49
2	Resorcinol	1.17
3	Ca3(PO4)2	1. 18
4	K ₃ PO ₄	1, 31
5.	Na ₃ SeO ₃	1. 34
6	No additive (UTX 8407)	1. 35
7	Sodium barbituate	1.37
8	Tetrabromophthalic anhydride	1. 51
9	Na ₃ PO ₄	1. 53

TABLE III

(U) EFFECT OF STABILIZERS AT ELEVATED TEMPERATURES

111 Days at 60° C

		Wt-% 1	Loss
UTX 8407		8.8	39
UTX 8407 + 2%	S	6. 4	42
UTX 8407 + 2%	urea	9. (04
UTX 8407 + 2%	LiF	10.	19

TABLE IV

(U) EFFECT OF BURNING RATE CATALYSTS ON STABILITY

67 Days at Ambient Temperature

	Wt-% Loss
UTX 8407	0.12
UTX 8407 + 1% milori blue	0. 38
UTX 8407 + 1% Fe ₂ O ₃	0. 62
UTX 8407 + 1% Fe ₃ O ₄	0.65
UTX 8407 + 1% Cu2O2	0.71
PBEP + TVOPA 50/50 (cured gumstock)	0. 34
PBEP (cured without TVOPA)	1.95

TABLE V

(U) WEIGHT LOSS THROUGH A 5-cm WEB 1-cm² x 5-cm LONG TUBE SAMPLES

Exposure Time = 200 Days

Formulation	Wt-% Loss at Ambient Temperature	Wt-% Loss at 45° C Temperature
UTX 8407 ^(1,2) (PBEP/TVOPA binder)	(a) 0.16 (b) 0.16	(a) 0.65 - sample swelled(b) 0.69 - sample swelled
Neat PBEP ⁽²⁾	0. 62	6. 42
UTP 8298 ⁽³⁾ (Uteflex/TMETN binder)	0. 044	0. 25
UTX 8410 ^(1, 2) (PBEP/DBP binder)	0. 16	0. 68
198-187 ⁽²⁾ (PBEP + DBP 50/50) (cured)	0. 10	3. 99

- 1. These samples contain 50% AP and 15% Al
- 2. PBEP lot 9165-107
- 3. Contains 16% Al, 66.4% AP

evaluated in UTX 8410. TVOPA was replaced by the less volatile DBP. No change in weight loss was observed by this variation.

2. (C) ALUMINUM HYDRIDE STUDIES

Evaluation of AlH3 in PBEP propellant was continued during this quarter. The primary work involved studies on the factors affecting the impact sensitivity of AlH3-containing propellants and on developing a good durable AlH3-HAP propellant. Among the factors which could affect the impact sensitivity of AlH3-PBEP propellant are PBEP sensitivity, the oxidizer concentration, and the TVOPA level. These variables were evaluated and the results are shown in table VI. In formulations 178-102-1 through 178-102-5, PBEP lot 9165-180, which had shown extremely good impact sensitivities in the range of 70 to 80 kg-cm, was evaluated with AlH, to determine if this would impart an improved impact sensitivity to the propellant. It can be seen that no significant improvement in impact was obtained by utilizing this lot of PBEP. In these studies two types of AlH, were evaluated - magnesium-doped material and acrylonitriletreated AlH2. Those mixes made with acrylonitrile-treated AlH2, in general, gave somewhat higher impact values. At this time it is not known if this is caused by an intrinsic characteristic of the hydride or if the difference is caused by micro-porosity which could have occured with the use of magnesium-doped AlH₂.

tVI

- (C) Previous experience with PEEP/TVOPA/AP/Al propellant has shown that addition of ammonium perchlorate (AP) resulted in an improved impact sensitivity. In formulations 178-102-6 through -8, the effect of the addition of AP is shown. No improvement in impact sensitivity was noted with addition of AP oxidizer. No effect attributable to concentration of AP was observed. Again, in these mixes notably between -6 and -7 an improvement in impact sensitivity is observed by use of acrylonitriletreated AlH₃.
- (C) In formulations 178-105-1 through -4, the effect of TVOPA concentration was evaluated. Formulations 178-105-1 and -2 were the controls with a PBEP/TVOPA ratio of 1 to 2 and 1 to 3, respectively. For some reason, these formulations with the increased TVOPA level gave a somewhat lower impact sensitivity in the uncured state than did the 1/1 PBEP/TVOPA binder. No improvement in impact sensitivity was obtained in the uncured propellant, although the cured propellant in one case did give a slightly improved impact sensitivity. In all cases an improvement in impact sensitivity was obtained with the cured propellant. At this time there does not appear to be any easy method of improving the impact sensitivity of AlH₂-containing propellant.

(U) LMH-1 IMPACT DATA⁽¹⁾

178-	80	50(3)	i	2.	0.4
178-	80	20(3)	;	2. 2	0.9
178-	1/3		}	41	40
178-	100	1	}	15	32
178-	47.7	10. 1(3)	42. 2	2.5	6.9
178-	57. 2 1/1	13.5(3)	29.3	o	2.4
178-	56.4	15. 2(2)	28.4	2.0	 6
178-	83.0 1/1	17. 0(3)			ر. 0
178-	88.6	11. 4(2)		2.0	 8
178-	84. 2	15.8(3)		რ	2.4
178-	91.6	8.4(2)	1	 	3.0
173-	100	-1	-	27	0.2
Sample	Binder PBEP/ TVOPA Ratio	LMH-1	ΑЪ	Impact sensitivity E50 kg-cm (uncured)	Impact sensitivity E50 kg-cm (cured)

1. All values for ingredients are in wt-%.

2. Magnesium-doped LMH-1.

- (C) Because impulse and density improvements are obtained by substituting HAP for AP in the AlH₃/PBEP system, a concurrent evaluation of these oxidizers is being performed. The diisocyanate, 3, 3'-dimethyl-phenylmethane-4, 4'-diisocyanate (DMM) previously gave satisfactory cures in HAP propellants. However, in-house work with HAP propellants has shown that some incompatibility exists between HAP and the cure catalyst FeAA. Accordingly, a series of hand mixes evaluating FeAA and DBTDA was prepared. Formulations tested are shown in table VII. Control mixes of Al-AP and Al-HAP were included in this study.
- (C) A color change from red to reddish brown was noted when HAP was added to the FeAA-containing binder. The mixes were stiff and gave a somewhat porous cure. However, propellant containing DBTDA were fluid and cured to a firm-rubbery propellant. The presence of AlH3 in these mixes appeared to have no effect on the cure. The curative utilized in these studies, DMM, is not currently commercially available. There is, however, sufficient material on hand at UTC to complete all requirements of this contract. A number of diisocyanates of similar structure and reactivities have been obtained and will be evaluated as alternates to DMM. It is felt that these other diisocyanates will be substitutable for the DMM without introducing the incompatibility that is observed with TDI and HAP.

3. BURNING RATE STUDY

- (C) One of the objectives of phase II of this program is to develop a series of domino-propellants with burning rates of 1.0 to 10.0 in./sec at 1,000 psi. The typical formulation, such as UTX 8407, has a burning rate of approximately 1.6 in./sec. Various combustion modifiers including the usual AP burning rate catalysts, binder decomposition catalysts, AP burning rate depressants, and polymer flame retardants are being tested. Also, high TVOPA-plasticized formulations which have high burning rates without added catalysts were examined. Initially, the compatibility and hazard characteristics of the NF₂ binder and these various additives were tested by DTA, impact, friction, spark, and autoignition tests.
- a. Effects of Ammonium Perchlorate Catalysts on Cure and Stability
- (C) DTA results have shown that AP burning rate catalysts decrease the exotherm onset and peak temperatures of PBEP. It was thought that the cure of the PBEP/TVOPA binder might also be affected by these burning rate catalysts.
- (C) Small hand mixes were made of UTX 8407 containing 1% catalyst to determine the compatibility of these additives in the propellant formulation and to determine the effects on cure. These formulations are listed in

(U) CURE CATALYST STUDY

Ingredient	178-109-1	178-109-2	178-109-3	178-109-4		178-116-1 178-116-2	178-116-3
LMH-1	16.7	18.5	1	-	1	11.6	10.2
¥	-		20.7	20.5	11.5	1	1
HAP	33, 3	•	34. 5		!	23. 1	1
AP	:	37.0	!	34. 2	!	1	20.3
Binder	50.0	44.5	44.8	45.3	65.5	65.3	69.5
Cure catalyst	FeAA	FeAA	Fe.AA	FeAA	DBTDA	DBTDA	DBTDA
Triol/OH	1.4	1.4	1.4	1.4	1.4	2.7	1.4
NCO*/OH	1.5	1.5	1.5	1.5	1.5	1.0	1.5
Results	Firm cure	Firm cure	Firm cure	Soft cure	Firm cure	Firm cure	Firm cure
	Porous	Bubbles on surface	Bubbles on surface		Slight bubble formation		

* DMM diisocyanate used.

on surface

table VIII. The results indicate that Cu2O2, Fe₂O₃, Fe₃O₄, and Milori blue are compatible in UTX 8407 and cure well, while both CMB-3 and (Et) 4 NBr cured slowly into a spongy propellant. There appears to be a compatibility problem with these quaternary amines. Further studies will be required to determine if quaternary amines can be used in PBEP propellants. DTA results listed in table LX show that Fe₃O₄ does not decrease PBEP stability to any large extent, and Cu2O2 does decrease stability.

- b. Burning Rate Depressants Compatibility Studies
- (C) DTA studies have previously shown that most candidates for burning rate suppressants apparently increase the DTA stability of PBEP. Hand mixes of UTX 8407 formulation containing these additives, listed in table X, all gave good cures. These additives include such things as sodium barbituate as a burning rate depressant, tetrabromophthalic anhydride as a flame retardant, as well as others with similar properties.
- (C) Tricresyl phosphate and ammonium oxalate mixed with PBEP also were studied by DTA. The tricresyl phosphate-PBEP mixture gave no appreciable change in the thermogram when compared to the thermogram of neat PBEP. However, adding ammonium oxalate decreased the onset by about 20°C, the first exotherm peak by 52°C, and the second exotherm peak by 24°C. The oxalate was a monohydrate, and the water of hydration may have had some effect on the thermogram.
- (C) Table XI indicates that the several depressants tested in propellant formulations did not affect the friction or impact sensitivity of the propellant.
- c. High TVOPA Level Effect on Propellant Sensitivity
- (C) Reports have indicated that increasing the TVOPA level of a propellant will increase the burning rate. It was thought that thic higher TVOPA level would increase the impact and friction sensitivity of the propellant. Surprisingly, the results in table XI show just the opposite effect for impact. A TVOPA/PBEP ratio of 2:1 gave a value of 17.6 kg-cm and a 3:1 ratio gave a value of 20.5 kg-cm. This compares to a value of 11.8 kg-cm for a 1.1 ratio. The friction sensitivity remained essentially the same at all levels.
- d. Preparation of Strands for Burning Rate Evaluation
- (C) Several formulations, listed in table XII, for burning rate strands were prepared at the 100-g level in the ARC mixer. These included a mix containing Cu2C2 as an additive as well as formulations varying the particle size and TVOPA level. Table XII shows the burning rate at 1,000 psi, and the strand results are given in figure 2.



TABLE VIII

(U) EFFECT OF BURNING RATE CATALYSTS ON PROPELLANT CURE

LA 45-6	%66	1% Fe ₃ O ₄	Cured
LA 45-5	% 66	1% (Et)4NBr(3)	Cured slowly Forous
LA 45-4	%66	1% Milori blue	Cured
LA 45-3	%66	1% QMB-3(2)	Cured slowly Porous
LA 45-2	%66	1% Fe ₂ O ₃	Cured
LA 45-1	%66	: % Cu202	Cured
Formulation No.	UTX 8407(1)	Additive	Results

UTX8407 is PBEF/TVOPA/AP/Al cured with TDI and crosslinked with 1, 2, 6-HT
 Quaternary methyl ammonium triborate, Callery Chemical
 Quaternary ethyl ammonium boride

TABLE IX

(U) DTA RESULTS

Sample Composition	Onset ° C First Exotherm	Peak ° C First Exotherm	Peak ° C Second Exotherm	Endotherms
PBEP + K ₃ PO ₄ (75/25)	70	100	186	140, :177
PBEP (100)	146	204	219	1
PBEP + Cv2O2 (75/25)	96	152	:	1
PBEP + Fe ₃ O ₄ (75/25)	156	506	-	-
PBEP + NH4C2O4N2O (75/25)	127	152	195	114
PREP + tricresvi phosphate (75/25)	142	195	199	1

TABLE X

(U) EFFECT OF STABILIZERS AND BURNING RATE DEPRESSANTS ON PROPELLANT CURE

Formulation No.	UTX 8407 ⁽¹⁾	Additive	Results
LA 31-1	98%	2% LiF	Cured
LA 31-2	98%	2% S	Cured
LA 31-4	100%	0	Cured
LA 41-1	99.5%	0.5% Na ₃ PO ₄	Cured
LA 41-2	99.5%	0.5% K ₃ PO ₄	Cured
LA 41-3	99.5%	0.5% NaSeO ₃	Cured
LA 41-4	99 . 5%	0.5% tricresyl phosphate	Cured
LA 41-5	99.5%	0.5% tetrabromo anhydride	Cured
LA 41-6	99.5%	0.5% resorcinol	Cured
LA 41-7	99.5%	0.5% tricalcium phosphate	Cured
LA 41-8	99.5%	0.5% sodium barbituate	Cured

⁽¹⁾ UTX 8407 is PBEP/TVOPA/AP/Al cured with TDI and crosslinked with 1, 2, 6-HT.

TABLE XI

(U) HAZARD EVALUATION RESULTS

	Impact				
Formulation No.	Sensitivity kg-cm	No Grit	Diamond Grit	Pyrex Grit	Remarks
UTX 8407	11.8	-	+	+	1:1 TVOPA/PBEP
UTX 8476-1	17.6	•	+	+	2:1 TVOPA/PBEP
UTX 8477-1	20.5		+	+	3:1 TVOPA/PBEP
LA 41-5	12.0		•••		1% tetrabromo phthalic anhydride
LA 41-4	11.5				1% tricresyl phospahte
LA 41-8	13.0				1% sodium barbituate
	The second contract of				

- (C) Formulations UTX 8482 and UTX 8481 had some porosity which may have contributed to their high rates. A burning rate of 2.6 in./sec at 1,000 psi was obtained in formulation UTX 8482 containing 1% Cu202 and a 4:1 ratio of fine to coarse AP. Using all coarse AP (350µ) in formulation UTX 8480 resulted in only a decrease of 0.06 in./sec from the standard formulation UTX 8478.
- (C) Current efforts to obtain lower burning rates will be devoted to methods of decreasing the burning rate of the binder by using some of the stabilizers discussed in section I.

4. SURVEILLANCE PROGRAM

- (C) Under phase III of this program, the aging characteristics of PBEP propellant are being studies in a long-term surveillance program. Burning rate strands, 1-lb motors microbone test samples, and diffusion vials will be conditioned and periodically sampled for testing and evaluation. Test conditions of 24° C for 2 years and 35° C for 1 year are being used. Data on changes in burning rate, specific impulse, tensile properties, and weight loss will be obtained.
- (C) The microdogbones and six 1-lb motors have been prepared and placed in storage. Because of the cure difficulties encountered in scaleup (this problem is discussed in detail in section II, part 5), completion of propellant processing for this phase has been delayed.

(U) STRAND BURNING RATE FORMULATIONS

Formulation No.	UTX-8478	UTX-8479	UTX-8480	UTX-8481	UTX-8482
PBEP	15.70	15.70	14.70	10.47	10.37
TVOPA	15.70	14.70	14.70	20.93	20.72
TDI	1.84	1.84	1.84	1.84	1.82
1, 2, 6-HT	0.56	0.46	0.46	0.46	0.46
FeAA	0.65	0.39	0.39	6.39	0.39
A1	15.20	15.20	15.20	15.20	15.04
АР, 180	35.15	10.14	;	10.14	10.04
АР, 350µ	1		50.71	-	-1
AP, 8 - 10µ	15.00	40.57	;	40.57	40.16
Variable	Control	80/20 fine/coarse AP	350µ AP	2/1 TVOPA/PBEP	1.00% Cu2O2
rb, in./sec, at 1,000 psi	1.46	1.72	1.40	2.40	2.60
п	99.0	0.66	99.0	0.50	0.50

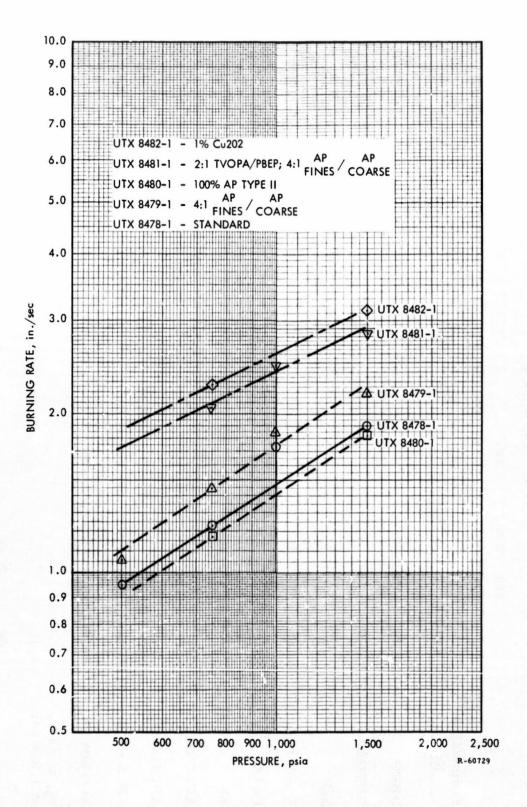


Figure 2. (U) Strand Burning Rate Data

- (C) In addition to the samples discussed above, two 2-in. cubes, shown in figure 3, were prepared for storage. One cube utilized FeAA cure catalyst, and the other cube used DBTDA. Failure criteria in these cubes will be determined by fissuring or void formation as determined by X-ray analysis.
- 5. PBEP PROPELLANT STUDIES
- a. PBEP/TVOPA Scaleup Studies
- (C) In the preparation of the 1-lb motors for the surveillance program, a number of mixes were scheduled in the 2-quart Bramley-Bekin mixer. However, a problem was encountered in this work in that these mixes failed to cure properly and exhibited signs of porosity. This problem was discussed in the last quarterly report, and the problem was reported as being caused by the formation of what was believed to be HF during the solvent removal step. A solution was proposed which involved vacuum degassing of the binder ingredients prior to addition of the FeAA cure catalyst. At that time the conditions leading to the lack of cure had been duplicated in the ARC mixer. It was felt that this was the solution to the problem.
- (C) It has now been established that this was only part of the problem, but that the total solution of the problem was not obtained by this change in technique even with utilization of the improved processing technique. Sporadic cures and gassing was obtained on the propellants prepared in the Bramley-Bekin mixer. A total of six 1-lb motors were obtained out of the Bramley-Bekin mixer. However, the propellant does not exhibit as good a consolidation as that routinely achieved in the ARC mixer. The propellant obtained from the Bramley-Bekin mixer since these early studies progressively worsened until extreme porosity and lack of cure in all Bramely-Bekin mixers was observed.
- (U) A systematic study of this problem was undertaken during this quarter on the effects of process variables such as order of addition of ingredients, mix temperature, cure temperature, and cure time. Also, studies involving sampling of the mix at selected intervals for analytical analysis to establish if residual solvent or degradation had occurred and evaluation of possible contaminates that could be appearing in the mix from the mixer itself.
- (C) Formulations evaluated during this quarter are given in table XIII. Two PBEP lots have been used during this study, 9546-16 and 9557-84. Table XIV lists the gumstock evaluation studies conducted with lot 9557-84. This is a study that is routinely performed on all new lots of PBEP to establish the optimum NCO and triol levels for that given lot. Experience has shown that the formulations evaluated as a control technique by Shell Chemical

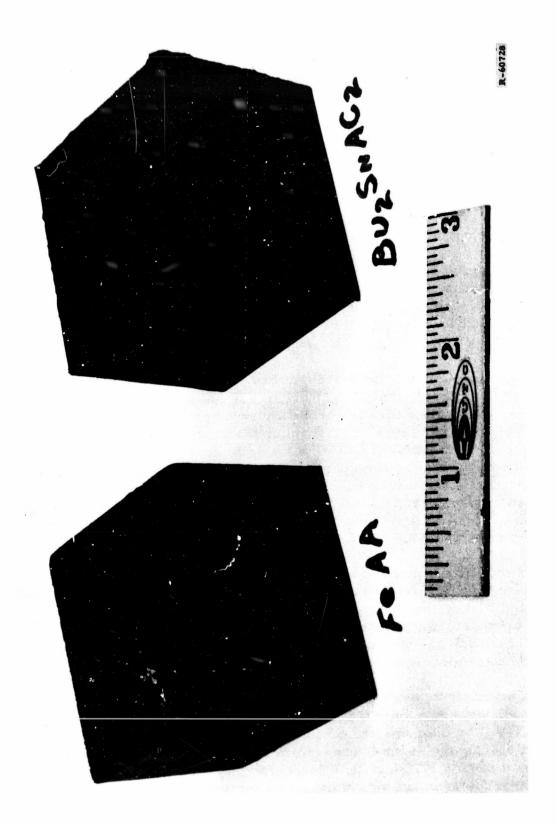


Figure 3. (U) Two-in. Cubes for Surveillance Study

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(U) SCALEUP FORMULATIONS(1) TABLE XIII

	UTX-	UT:C-				UTX-	UTX-			UTX-	UTX-	UTX-		UTX-
Formulation	8414-2	8415-1				8418-2	8417-2			8418-3	8418-4	8420-1		8421-2
PBEP	16.0(2)		16. 1(2)	16.05(2)	16. 02(2)	16.02(2)	16.05(2)	15.88(3)	15.88(3)	16.04(3)	16.04(3)	16.07(3)	18, 31(3)	18, 31(3)
TVOPA	16.0	_				16.02	16.05			16.04	16.04	16.07		18.31
TDI	1.914	1.915				1.914	1.914			1.92	1.92	1.92		2. 20
1. 2. 6-HT	0.437	0.438				0.438	0.438			0.44	0.44	0.43		0.50
FeAA	0.640	0, 100				0.400	0.300			0.40	0.40	0. 20		0.51
14	15.0	15.1				15.00	15.00			15.04	15.04	15.07		13.03
AP	50.0	50.4				50.15	50. 25			50. 12	50.12	50. 24		47. 23
Triol/PBEHOH)	1.55	1.55				1.55	1.55			1. 00(4)	1.00(4)	1.00(4)		0.85(4)
NCO/OH	1.30	1.30				1.30	1.30			1.07(7)	1.07(=)	1.07(1)		0.985(1)
Cure at 120 ° F (hr)	24	120				7.2	7.2			72	72	144		7.2
Remarks	Well	Uncur ed				Cured	Cured			Well	Well	Uncured		Well
	cured									cured	cured			cured
	UTX-	UTX-							UTX-	UTX-	UTX-	UTX-	UTX-	uTX-
Formulation	8421-3								8422-6	8422-7	8477-8	8422-9	8422-10	8423-1
PREP	18, 31(3)	18, 31(3)	18, 31(3)	18.31(3)	(3) 18, 31(3)		18.31(3)	18.31(3)	is. 31 ⁽³⁾	18.31(3)	18.31(3)	18.31(3)	18.31(3)	1., 31(3)
TVOPA	18.31	18.31							18.31	18.31	18.31	18.31	18.31	18.31
TDI	2. 20	2. 18							2. 18	2. 18	2. 18	2. 18	2. 18	2. 18
1, 2, 6-HT	0.50	0.50							0.50	0.50	0.50	05.0	0.50	0.50
FeAA	0.51	0.64							0.64	0.64	0.64	0.64	0.54	0.64(2)
W	13, 30	13.01							13.01	13.01	13.01	13.01	13.01	13.01
AP	47. 23	47.05							47.05,4	47.05	47.05	47.05,4)	47.05	47.05
Triol/PBEP(OII)	0.85(4)	0.85(4)							0.85(4)	0.85(4)	0.85	0.85	0.85(4)	0.85(4)
NCJ/OH	0.985	0.977(0.977(1)	0.977(=)	0.977(1)	0.977	0.977	0.977
Cure at 120 ° F (hr)	7.2	7.5			u		_		72	7.2	96	120	96	72
Remarks	Well	Well	Well		b		2		Uncured	Cured	Uncured	Uncured	Cured	Cured
	cared	cared	cared											
	spion			voids										

TABLE XIV
(U) PBEP LOT EVALUATION FORMULATIONS (1)

Formulation	215-76-1	215-72-2	215-76-3	215-74-6	215-76-5
PBEP ⁽²⁾	46.1	45.8	45.2	44.6	44. 45
TVOPA	46.1	45.8	45.2	44.6	44. 45
TDI	5.58	6.06	7. 15	8.26	8.26
1,2,6-HT	1.30	1.48	1.54	1.41	1.74
FeAA	0.92	0.91	0.91	0.90	0.90
Triol/PBEP(OH)(3)	0.95	1.00	1.00	1.00	1.30
$NCO/OH^{(3)}$	0.95	1.00	1.20	1.40	1.40
Cure at 120° F (hr)	24	24	72	96	72
Remarks	Cured	Cured	Cured	Cured	Cured

- 1. All values for ingredients are in wt-%.
- 2. PBEB lot was 9557-84.
- 3. The triol/PBEP(OH) and NCO/OH ratios are based on 0.075 hydroxyl equivalents per 100 g of polymer determined by gel time studies rather than a value of approximately 0.041 as determined by IR.

on these lots have exhibited satisfactory properties in the PBEP/TVOPA/AP aluminum propellant systems. In general, triol-to-dioland NCO-to-OH ratios have been chosen in the middle ranges of those evaluated by Shell.

(C) In table XIV it can be seen that good cures were obtained with lot 9557-84 of PBEP with NCO-to-OH ratios varying from 0.95 to 1.40 and with triol-diol ratios from 0.95 to 1.30. The cure was more rapid at the lower equivalents level, although ultimately all samples reached approximately the same degree of cure and exhibited approximately the same physical properties. Because it is advantageous to use as short a cure time as possible and still have adequate pot life for formulation work, formulations around an NCO-to-OH level of approximately 1.0 were used. The triol-to-diol and NCO-to-OH ratios currently used are based on an 0.075 hydroxyl equivalent for 100 g of polymer as determined by gel time studies by Shell Chemical rather than a value of approximately 0.041 as determined previously by Shell Chemical by IR techniques. This technique appears to be the much more reasonable method of evaluating the hydroxyl equivalents of PBEP than the previously used IR and allows formulation of PBEP along more conventional polyurethane calculation techniques.

- One of the variables evaluated was that of cure catalyst level in formulations UTX 8415 through UTX 8418-2. The FeAA catalyst level was varied from 0. 1% to 0.4%. All formulations cured with the exception of the 0.1% catalyst level. These mixes were prepared in the ARC mixer without difficulty, and they gave extremely good-looking propellant with good physical properties. These formulations gave tensile properties ranging from 158 psi to 210 psi and elongations of 25% to 20%. Two mixes were prepared in a gallon Baker-Perkins mixer, UTX 8418-1 and UTX 8417-2, for 1-lb motors. However, these mixes were not castable through the valving system used on this mixer. The propellant that did come out, however, appeared to cure satisfactorily.
- Following these mixes, a switch in PBEP lots to 9557-84 was made, and the ARC mixes carried out to check the cure characteristics of this propellant in UTX 8419. Good cures were obtained with this PBEP lot, with measured physical properties of 100 psi and 23% elongation being obtained. Because the gallon mixer could not be adapted to the research studies on this system, further formulation studies were conducted using the Bramley-Bekin mixer. Formulation 8420-1, which was prepared in the Bramely-Bekin mixer, failed to cure.
- At that time it was believed that possibly this was caused by the marginal cure catalyst level of 0.2%. Accordingly, two Bramley-Bekin mixes were prepared in UTX 8421-3 and UTX 8421-4 from the Bramley-Bekin mixer. Propellant obtained from these mixes did cure. However, some voids were observed. The voids appeared primarily to be surface voids with some bubble formation observed where the propellant was in contact with the mandrel. Following these mixes, subsequent mixes prepared in the Bramley-Bekin mixer failed to cure, giving only surface cures in cube specimens. The outer six sides of the cube would cure uniformly to a depth approximately 1/4 to 3/8 of an in. with the inner propellant being completely uncured and highly porous. Because there was a suspicion that the solvent might not be completely removed from the propellant, an extended solvent removal at 50° C was evaluated. This mix, UTX 8422-5, showed even more extreme gassing and lack of cure than had previously been noted. It appeared evident, therefore, that this was moving in the wrong direc-Accordingly, a mix was made where an abbreviated solvent removal step was utilized. This propellant still failed to cure properly and exhibited gassing but was somewhat improved over the extended solvent removal formulation.
- In one of the tests evaluated, samples of the binder were periodically removed at hour intervals and tested for presence of solvent both by weight loss measurements and analytical IR and chlorine analysis. It was established by this technique that the solvent removal procedures were satisfactory

in lowering the solvent content to a degree that no further solvent removal was observable under vacuum and heat application. At this point the processing of the propellant continued with the addition of fuel, oxidizer, and curatives; and again the propellant failed to cure properly and exhibited gassing. This apparently eliminated the possibility of residual solvent as being the cause of the problem.

- (C) To evaluate the possibility that contaminates from the mixer head were leaking into the propellant during the solvent removal step where solvent vapors could permeate the grease in the mixer head, a sample of the binder was taken following solvent removal in the Bramley-Bekin; transported to the processing cell containing the ARC mixer; the propellant processing continued then in the ARC; and the formulation processing continued in the Bramley-Bekin. The mix completed in the ARC mixer cured giving very good, nonporous propellant; whereas, gassing and lack of cure were again observed in the propellant processed from the Bramley-Bekin mixer. In these tests all ingredients are, of course, taken from the same lots so that no variation in ingredients is possible. Analytical analysis for TDI and hexanetriol show that this, also, was not a factor in this variation in cure.
- (C) Because the processing carried out in the ARC mixer is approximately 9° Flower intemperature than that in the Bramley-Bekin mixer, the temperature in the Bramley-Bekin mix pot was lowered to correspond to that of the ARC mixer. Both mixes then were carried out using the same time of solvent removal and processing time. Again, the same results as previously described were obtained, good, well-consolidated, thoroughly cured propellant in the ARC mixer, uncured propellant in the Bramley-Bekin. To eliminate variables in cure, samples of Bramley-Bekin propellant were cured both in the ovens normally used with the Bramley-Bekin process cells and in those used with the ARC process cells. No variation in results was obtained in this test; both samples of propellant failing to cure and exhibiting porosity.
- (C) To check on the possibility of grease contaminates from the mixer head getting into the mix, samples of the packing grease and the molybdenum disulfide in the grease were tested in the laboratory to determine their effect on the cure of the PBEP propellant. When molybdenum disulfide was added to the PBEP propellant, the color was removed from the molybdenum disulfide indicating some reaction occurred. However, the contaminated propellant continued to cure and exhibited only a minor amount of porosity not varying in degree from the control hand mix. The silicone grease used as a lubricant decolorized the binder somewhat but again did not affect the cure of the binder. To eliminate the effect of the silicone grease which

could react with any HF products from the binder, the mixer head was repacked with a fluorocarbon grease. No indication of grease leakage was observed, however, and it is not felt that this is a contributor to the problem.

- All tests performed indicated that there was no basic problem associative with either the formulation, PBEP, TVOPA, or any ingredients in the propellant that could be traced to the lack of cure. A complete reevaluation of the Bramley-Bekin processing controls and setup including such things as the vacuum lines, nitrogen purge line, etc., were carried out. The dewpoint of the nitrogen used was established as being -60° F, eliminating the possibility of moisture being introduced in this manner. Vacuum and nitrogen lines were checked, and auxiliary vacuum traps and by-pass valves were installed to prevent any possibility of solvent being carried back into the mix when the vacuum was broken. A complete checkout of the mixer was conducted, including a thorough evaluation of possible air leak sites. seals, and all connections. The pot for the mixer was checked for possible micro cracks that could be allowing process water to enter the propellant. During this phase, an air leak was found around the center plug on the mix pot of the Bramley-Fekin. As this plug is not used in any normal use of the mixer, usually it is not dismantled or worked on. It is a press fit plug with an O-ring seal. The presence of an air leak such as this would explain the observations made during the past studies. The plug was sealed with a silicone rubber sealant and rechecked for leaks. The pot was refinished to remove any possible contaminants that might have built up in the stainless steel of the pot walls. The casting valve also was checked and established to be satisfactory. The vacuum to the mixer was measured on a McCloud gauge as being 0.4 mm Hg. Following completion of this work, another mix was made in the Bramley-Bekin mixer. Some improvement was observed in that the propellant did cure on the inside, although the cure was poor and extreme gassing and discoloration had occurred.
- (C) A mix was also made in the ARC where solvent was added to the mix prior to casting to determine its effect on the propellant. One-percent solvent (taken from a bottle of TVOPA) was added to the completed mix, mixed in for 5 min, and then the system was placed under vacuum and vacuum cast into a 2-in. cube mold. This propellant exhibited the same cured characteristics as the Bramley-Bekin propellant. The outside wall cured, with the inside poorly cured and porous Residual solvent can, therefore, apparently have very deletorious effects on the propellant. There appears to be a problem associated with the presence of solvent that cannot be explained by vaporization of the solvent to form voids. The propellant that fails to cure properly is also discolored, has a strong obnoxious odor (not HF), and is very deliquescent. Normal propellant made in the ARC mixer has none of these characteristics.

- (C) The study of this problem is continuing with mixes scheduled to evaluate other lots of PBEP, as well as extended mix times and checkout of residual solvent in the binder prior to addition of solids and curatives to the binder.
- b. Impact Testing of PBEP Lot 9088-180
- (C) Previous impact sensitivity testing of PBEP lot 9088-180 at UTC had given values of approximately 80 kg-cm. This value was much higher than data for previous lots which normally ran between 14-28 kg-cm. Shell Development had obtained values for this lot of similar magnitude to other lots tested. Therefore, samples both in solvent and neat were exchanged by Shell and UTC for testing in each others facilities. All samples sent by UTC gave values at Shell similar to those previously obtained of about 16-17 kg-cm. Three samples were sent to UTC and tested at our facilities. The results are shown in table XV. One sample that had been stripped of solvent at Shell gave a value of 66 to 56 kg-cm, which is similar to values obtained previously. The sample sent to UTC in solvent and stripped at UTC gave an impact value of 17 kg-cm. These discrepancies will be checked further by coordination of testing methods between Shell and UTC.
- (C) The reproduction of methods of testing at UTC was checked by resubmitting a sample of PBEP lot 8976-182 that had given a value of 24.7 kg-cm 9 months earlier. A second value of 26 kg-cm was obtained which indicates not only a consistency of method, but also that this lot has remained at about the same impact sensitivity for at least 9 months.
- c. Hazard Data
- (C) Data listed in table XV indicate that PBEP lot 9557-84 with an impact value of 28.0 kg-cm and autoignition temperatures of 525° and 475° F is comparable in hazard characteristics to normal PBEP lots.
- (C) Cured propellant containing lot 9456-16 had an impact value of 17.8 kg-cm and autoignition temperatures of 520° and 420° F which are similar values to many cured propellants containing other PBEP lots. UTX 8419-2 containing lot 9557-84 had an impact value of 7.5 kg-cm which is somewhat lower than usual, but autoignition values of 540° and 455° F are similar to values from other propellants. Although the value of 7.5 kg-cm is somewhat low, impact data for propellants containing other lots have been as low as 8-9 kg-cm.

TABLE XV

(U) HAZARD DATA

		Impact	Autoigni	tion Data F
Formulation No.	PBEP Lot	Sensitivity kg-cm	10 sec	30 sec
Pure PBEP	9557-84	28.0	525	475
UTX-8411-16	9456-16	17.8	520	420
UTX-8419-2	9557-84	7.5	540	455

Impact		to the same of the first
Sensitivity kg-cm	PBEP Lot	Remarks
80(1)	9088-180	UTC sample - stripped of solvent at UTC
59(1)	9088-180	UTC sample - stripped of solvent at UTC
73(1)	9088-180	UTC sample - stripped of solvent at UTC
70 ⁽²⁾	9088-180	UTC sample - stripped of solvent at UTC
66	9695-98C	Shell sample - strippedof solvent at Shell
56	9695-9EB	Shell sample - stripped of solvent at Shell
17	9088-180	Shell sample - stripped of solvent at UTC
24.7	8976-182	Tested in October 1965
26	8976-182	Tested in August 1966

- 1. This data collected over approximately a three month time period.
- 2. Portion of stripped sample sent to Shell for testing. Shell reported an impact of approximately 16 kg-cm for this material.

d. Tensile Properties

- (C) Several formulations had been tested previously for the necessary level of catalyst to obtain good cures and as a check on process variables. The tensile data listed in table XVI are from microdogbones obtained from these studies. The UTX \\411 series was a test on process variables, and the latter formulations varied only in FeAA level.
- (C) The tensile values were quite high in all cases varying from 100 to 240 psi. The elongation varied from 11.5% for UTX 8411-6 to 25.0% for UTX 8416-1. UTX 8411-5 and UTX 8411-6 both had some voids which probably accounts for their low elongation values.
- e. Temperature Effect on Physical Properties
- (C) Formulation UTX 8418, listed in table XIII, was tested at temperatures ranging from -10° F to -54° F. The data listed in table XVII indicate that the major changes in tensile properties for this propellant formulation are between -20° and -30° F. The values for both tensile and elongation are essentially the same at -30° and -54° F. Between -30° and -20° F both tensile and elongation values increase by a factor of about 2.5, indicating that the material changes from a glass to a cold plastic somewhere in this range. Further data are being obtained at temperatures between -10° F and 120° F to allow graphical analysis of change in tensile with temperature for this formulation.

TABLE XVI
(U) TENSILE PROPERTIES

		Meas	red Data	
Formulation No.	% FeAA	Tensile psi	Elongation %	Temperature ° F
UTX-8411-4	0.64	160	17.3	+76
UTX-8411-5	0.64	240	12.8	+76
UTX-8411-6	0.64	213	11.5	+76
UTX-8416-1	0.20	158	25.0	+76
UTX-8417-1	0.30	164	20.8	+76
UTX-8418-1	0.40	210	20.4	+76
UTX-8419-1	0.32	100.1	23.2	+76

TABLE XVII (U) VARIANCE OF TENSILE PROPERTIES WITH TEMPERATURE

		Cross	head Data
Formulation No.	Temperature F	Tensile psi	Elongation %
UTX-8418-3	-5%	288	2.0
UTX-8418-4	-30	371	1.7
UTX-8418-4	-20	911	5.2
UTX-8418-4	-10	727	15.9

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SECTION III

CONCLUSIONS AND FUTURE WORK

- (C) Additives which markedly improve the thermal stability of PBEP propellant have been found. However, further studies are required to define both the level of stabilizer required and whether using these additives in combination will offer further improvement.
- (C) Aluminum hydride continues to look promising in PBEP propellant both with AP or HAP as the solid oxidizer.
- (C) High burning rate propellants can be obtained in PBEP propellants using conventional techniques. However, to obtain a low burning rate propellant will require development of techniques to reduce the basic high burning rate attributable to the binder.
- (C) Further laboratory studies on PBEP stabilization are being conducted. The best stabilizers from these studies will be incorporated into the surveillance program. The AlH₃ studies are continuing, and scaleup of this system is planned. Studies on the cure problem encountered on scaleup are continuing. Efforts to define the source of this problem as well as the solution to it will be made.
- (C) Difficulties encountered in scaling up the PBEP propellant remain unresolved. There appears to be no intrinsic property of the system to prevent its scaleup.

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Sunnyvale, California		4	UP
3. REPORT TIPLE			
(U) EVALUATION OF HIGH-	ENERGY BINDE	R	
4. DESCRIPTIVE HOYES (Type of report and inclusive date:		A	10//
Second Quarterly Report, 1 June 1	1966 through 31	August	1966
	gai, Robert M.		
	a, Leo K.		
September 1966	76. VOTAL NO. OF	PAGES	O REPS
SA. CONTRACT OR GRANT NO. SA. ORIGINATOR		REPORT N	MBER(E)
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18. AVAILABILITY/LIMITATION NOTICES In addit		A STATE OF THE STATE OF	ments which must be
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11. SUPPLEMENTARY NOTES	ts. sponsoning M	LITARY AC	TIMITY Propulsion Laboratory
N/A	Research	nd Tech	nology Division Command, USAF ia
18. ABSTRACT			
(U) Thermal stability of PBEP and of the curative or crosslinks, and a weight loss of PBEP and PBEP pro-	most burning rat pellants. The e	e cataly	ysts increased the

Burning rate studies gave a burning rate of 2.0 in./sec at 1,000 psi in a catalyzed PBEP propellant. Cure problems were encountered in scaling up PBEP propellant to a two-quart mixer. Work is continuing to achieve a satisfactory cure.

Security Classification

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	KEY WORDS	ROLE	WT	ROLE	WT	ROLE	WT
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